

Variability of Heavy Metals in Wild Catfish *Clarias gariepinus* Collected South and North Cairo Area.

II. Essential Heavy Metals.

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ABSTRACT

Four surveys were undertaken to investigate the bioaccumulation of Fe, Cu, Zn and Mn in the liver, kidney, gills, skin and muscles of *Clarias gariepinus* from the River Nile south (Al-Aiat) and north (Barrage) areas of Cairo. Metals bioaccumulation were analyzed then applied to differentiate between the concentrations found at the two locations, between all of the surveys, and the two sexes.

No significant seasonal variations detected in the water metals. Fe and Cu are the highest elements and Mn is the least element. Cu is the more element affected by the locality with higher concentrations in Al-Aiat than Barrage. No hazardous effect on the environmental ecosystem observed.

Higher concentrations of metals were observed in the tissues of *C. gariepinus* than the water in which they live. All heavy metals in all organs are present in measurable quantities and still within the safe limits for consumption.

Concentrations of the analyzed metals revealed large numbers of significant values concerning location, sex and season differences. Discussion is focused on the significant results.

Key words: *Clarias gariepinus*, Iron, Copper, Zinc, Manganese, Season, Location, Sex.

INTRODUCTION

Iron, copper, zinc and manganese are classified as essential heavy metals in human diet because they all play significant roles in metabolic processes (Janssens *et al.*, 2009). These metals are also known to help in the growth and production of aquatic life. Alternatively, these minerals may be harmful to aquatic life, either through acute toxicity or chronic effects from accumulations in the organism over extended periods.

Intense activity in the industrial and agriculture sectors has led to the increased discharges of heavy metals in natural waters (Barlas, 1999 and Jordao *et al.*, 2002). According to Mathis and Kevern (1975), because fish are at the higher levels of the food-web and are usually eaten by man, they are the most sensitive group and used as an indicator of metal bioaccumulation in polluted waters. Many heavy metals are concentrated at different levels in different organs of the body (Rao and Padmaja, 2000) and when metals reach sufficiently high concentrations in body cells they can alter the physiological functioning of the fish (Heath, 1987). For these reasons, it is important to determine the concentrations of heavy metals in commercial fish in order to evaluate the possible risk of fish consumption for human health (Cid *et al.*, 2001).

Copper is one of the most abundant trace metals and for almost all organisms it is an essential micronutrient (Duffus, 1980). It has numerous functions in cellular biochemistry including vital roles in cellular respiration, and as a cofactor for over 30

different enzymes (Gatlin *et al.*, 1989). Copper is used today as a chemotherapeutic agent in aquaculture (Leatherland and Woo, 1998), but it is also toxic in excess (Handy, 1996). It increased coughing frequency, ventilation rate and oxygen consumption, decreased antibody production, decreased osmolarity and plasma Na levels, disrupted transepithelial ion exchange, inhibited Na-K-ATPase activity, reduction in viral clearance (Sellers *et al.*, 1975), stomach and intestinal distress, liver and kidney damage, and anemia (USEPA, 1991). It can also destroy both chemoreceptors and mechanoreceptors, and this renders the fish incapable of avoidance behaviour (Gardner and LaRoche, 1973). The harmful toxicity is largely attributed to its cupric (Cu^{2+}) forms which is the specie commonly found (Olaifa *et al.*, 2004_a). The increase in Cu pollution can be attributed to geological weathering, atmospheric deposition, municipal and industrial sewage, the discharge of mine tailings and fly ash (the major source of solid Cu pollution), fertilizer production and algaecide and molluscicide runoff (Moore and Ramamoorthy, 1984).

It is commonly accepted that Zn is an essential micronutrient required for normal growth and metabolic functions by various fish species (Gatlin *et al.*, 1991). Waalkees (1998) reported that a zinc concentration in fish was significantly correlated with traffic density adjacent to highways. As Cu, domestic sewage, chemical manufacturing, painting and coating, mining operations, extractive metallurgy, nuclear and other industries also release heavy metals to the environment (Jarup, 2003).

Iron is an essential trace element for haemoglobin formation (Friberg *et al.*, 1986), respiratory enzymes (Wetzel, 1983), normal functioning of the central nervous system and the enzymatic pathways of carbohydrate, protein and fat (Adeyeye and Otokiti, 1999). The main source of increased Fe concentrations in the aquatic environment is acid mine drainage, mineral and steel processing and industrial runoff (Förstner and Wittmann, 1983).

Manganese is an important component of many metabolic processes, including the functioning of flavoproteins and the synthesis of mucopolysaccharides, cholesterol and haemoglobin (DWAF, 1996). Beliles (1979) pointed out that the major sources for manganese as air and water pollutant are iron and steel manufacturing and the burning of diesel fuel in the motor cars.

The present study was, therefore undertaken to acquire information about the essential heavy metals (Fe, Cu, Zn and Mn) contents of natural carnivorous catfish (*Clarias gariepinus*) populations from two different study sites along the River Nile in the Cairo capital area. *C. gariepinus* was chosen based on the social and economic values in Egypt. Although only muscles of the fishes are eaten, samples of inedible tissues (liver, kidney, gills and skin) were also analyzed in order to establish a baseline for future studies of heavy metal pollution. The results were used to test for the effects of locality of capture, sex of fish, seasonal difference and types of tissue of the fishes on their heavy metals contents.

MATERIALS AND METHODS

Field collection:

Two main study sites (Fig. 1) of the River Nile were focused on during this study. The first site, Al-Aiat, is situated on the southern border of the Cairo Capital in close proximity to the industrial town of Helwan. The second site, Barrage, is situated approximately 100 km northern Al-Aiat in close proximity to the industrial town of Shubra El-Khaymah. Samples of *Clarias gariepinus* were caught by fishermen using

trawling nets and collected directly by the researchers from both areas. Fish were captured at the same time of collecting the water samples. Fishing trips to the studied areas were carried out every three months over a period of one year during 2008.

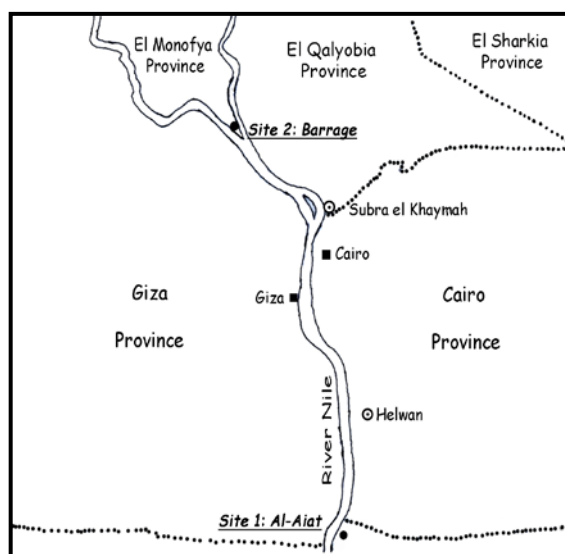


Fig. 1: The location of the two sites studied on the River Nile.

Four water samples from each locality were collected by a Hydro-Bios TPN water sampler at one meter depth as described by Parker (1972) in clean bottles of 1 liter capacity. The water samples were preserved by addition of 1 ml concentrated nitric acid until the time of analysis of heavy metals. The water samples from each site were filtered and kept at 4°C until analysis.

All fish were transferred alive in its water into holding tanks to the Animal Health Research Institute. After 24 hours, in the laboratory, measurement of fish standard length was carried out before sampling the organs of fish. The number of fish collected each season and the average total body length (cm) from both fishing sites are outlined in Table 1.

Table 1: Mean ± Standard deviation of the total body length (cm) of *Clarias gariepinus* collected from Al-Aiat and Barrage regions.

	Winter season January		Spring season April		Summer season July		Autumn season October	
	Male	Female	Male	Female	Male	Female	Male	Female
Al-Aiat region:								
No. of samples	11	8	8	8	13	7	11	11
Range	25 – 43	25 – 37	31 – 41	29 – 39	22 – 36	28 – 33	26 – 37	22 – 38
Mean	35.6	34.5	34.7	36.3	31.9	31.1	31.4	30.9
S.D. ±	5.482	4.000	3.348	3.059	4.375	1.676	3.749	4.721
Barrage region:								
No. of samples	10	11	8	8	8	11	12	7
Range	31 – 40	23 – 34	34 – 40	31 – 42	27 – 34	25 – 37	27 – 40	28 – 39
Mean	35.2	30.6	36.8	35.9	31.1	30.8	32.8	31.6
S.D. ±	2.974	2.911	2.188	3.300	2.295	4.094	4.366	3.780

Each fish was washed with deionized water and dissected to obtain liver, kidney, gills, skin and muscles. The muscle and skin tissue samples were taken from above the lateral line, at the beginning of the dorsal fin in each fish and as deep as the backbone. Gill filaments were removed from the cartilaginous gill arches. After

dissection, the tissue samples were minced and homogenized separately. The samples were placed on clean dry glass plates and dried in an oven at 105 °C for 48 hours (Bohn and McElroy, 1976). The dry samples were wrapped in aluminium foil and stored until metal analysis.

Analytical methods:

Before use, all glassware and plastic utensils were previously soaked overnight in 5 M HNO₃ and rinsed with deionized water. One gram of dry samples of the liver, kidney, gills, skin and muscle were digested separately in glass tubes with 10 ml of acid mixture (nitric acid/perchloric acid; 7:3 v/v). The digestion was facilitated by heating at 70°C. After cooling, all digests were filtered through a Whatman 42 filter paper, and then diluted with deionized water to give a final volume of 25 ml.

A Unicam 969 Atomic Absorption Spectrometer with acetylene/air flame was used in accordance with the manufacturer's specifications for the determination of Fe, Cu, Zn and Mn within the digested samples and filtered water (Wood and Van Vleet, 1996).

The percentage of change of metal concentration in a particular organ from Al-Aiat (site I) to Barrage (site II) areas was determined according to the following formula: [(Conc. at site II - Conc. at site I) / Conc. at site I] X 100

Statistical analysis:

Results were expressed as means ± standard deviation. Comparisons of means were performed with *t*-tests (Snedecor, 1971). For the smaller subset of data on the bioaccumulation of heavy metals in each tissue, analysis of variance (ANOVA) was used to compare seasonal variability with a fiducially limiting of 5 % (EpiInfo 6.2 and SPSS 8 Softwares). Microsoft excel was used to plot the graphs of the percentage change of heavy metals concentrations in each tissue between the two sites studied.

RESULTS

Water analysis:

Range, mean and standard deviation of Fe, Cu, Zn and Mn concentrations in the water samples collected from Al-Aiat and Barrage areas in the four seasons are summarized in Table (2). No significant differences were detected in the concentrations of the four elements between the different seasons. Copper concentration significantly differed in autumn ($P < 0.05$) and winter ($P < 0.01$) between the two localities with higher concentrations in Al-Aiat area than Barrage. Iron and zinc concentrations were significantly ($P < 0.01$) increased in Barrage area than Al-Aiat at spring season. Manganese concentration showed significant ($P < 0.001$) higher value in Al-Aiat area than Barrage at summer season.

Tissue analysis:

The five different tissue type's liver, kidney, gills, skin and muscles were analyzed for the four metals specified and the results for both localities were summarized and tabulated (Tables 3 - 6). There is a large amount of variation amongst the different tissues with regard to each metal. Therefore, the results for each metal will be explained individually.

1) Effect of Location:

Iron (Table 3 and Figs. 2 & 3):

At winter, Fe content was significantly ($P < 0.05$) decreased in the liver of female *Clarias gariepinus* collected from Barrage area than Al-Aiat (percentage of change: 35.5 %, Fig. 3). At autumn, both sexes showed significant differences between the two localities with lower and higher values of liver Fe in male (37.2 %) and female (82.7 %) respectively collected from Barrage than Al-Aiat (Figs. 2 & 3). In kidney, the only significant ($P < 0.05$) value was showed in female fish at spring season with higher value in Barrage than Al-Aiat (53.9 %, Fig. 3).

Table 2: Range, mean and ± standard deviation of iron, copper, zinc and manganese ($\mu\text{g l}^{-1}$) of water samples collected seasonally from Al-Aiat and Barrage areas.

Season		Al-Aiat area (4)			Barrage area (4)		
		Range	Mean	± S.D.	Range	Mean	± S.D.
Winter	Fe	0.0421 – 0.0910	0.0666	0.0282	0.0228 – 0.0697	0.0463	0.0271
	Cu	0.0511 – 0.0576	0.0544	0.0038	0.0438 – 0.0440	0.0439	0.0001 ^b
	Zn	0.0032 – 0.0093	0.0063	0.0035	0.0068 – 0.0089	0.0079	0.0012
	Mn	0.0259 – 0.0272	0.0266	0.0008	0.0079 – 0.0373	0.0263	0.0141
Spring	Fe	0.0182 – 0.0208	0.0195	0.0015	0.0951 – 0.1656	0.1304	0.0407 ^b
	Cu	0.0452 – 0.0597	0.0525	0.0084	0.0158 – 0.0541	0.0350	0.0221
	Zn	0.0018 – 0.0036	0.0027	0.0010	0.0074 – 0.0116	0.0095	0.0024 ^b
	Mn	0.0229 – 0.0579	0.0404	0.0202	0.0074 – 0.0294	0.0212	0.0105
Summer	Fe	0.0186 – 0.0432	0.0309	0.0142	0.0316 – 0.1096	0.0706	0.0450
	Cu	0.0447 – 0.0487	0.0467	0.0023	0.0403 – 0.0666	0.0535	0.0152
	Zn	0.0001 – 0.0031	0.0016	0.0017	0.0002 – 0.0092	0.0047	0.0052
	Mn	0.0185 – 0.0219	0.0202	0.0020	0.0047 – 0.0080	0.0064	0.0019 ^c
Autumn	Fe	0.0133 – 0.1741	0.0937	0.0928	0.0049 – 0.1568	0.0629	0.0657
	Cu	0.0457 – 0.0474	0.0466	0.0010	0.0362 – 0.0440	0.0401	0.0032 ^a
	Zn	0.0018 – 0.0073	0.0046	0.0032	0.0055 – 0.0182	0.0094	0.0060
	Mn	0.0253 – 0.0473	0.0363	0.0127	0.0082 – 0.0272	0.0201	0.0091
ANOVA	Fe	N.S.			N.S.		
	Cu	N.S.			N.S.		
	Zn	N.S.			N.S.		
	Mn	N.S.			N.S.		

Significant difference between two areas: a: $P < 0.05$ b: $P < 0.01$ c: $P < 0.001$

Table 3: Mean ± standard deviation of iron concentration ($\mu\text{g g}^{-1}$ dry weight) in different tissues of both sexes of *Clarias gariepinus* collected from Al-Aiat (site I) and Barrage (site II) areas during the four seasons.

Tissue	Site	Winter		Spring		Summer		Autumn		ANOVA	
		Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Liver	I	943.4 ± 328.0	1353.1 ± 374.6*	355.8 ± 145.8	296.2 ± 103.5	402.5 ± 201.6	642.6 ± 320.7	956.2 ± 364.5	578.9 ± 277.6*	$P < 0.01$	$P < 0.01$
	II	979.5 ± 397.0	872.3 ± 415.3 ^a	309.5 ± 177.3	434.7 ± 195.5	483.8 ± 205.6	470.3 ± 220.0	600.3 ± 298.1 ^a	1057.5 ± 408.3 ^{ab}	$P < 0.05$	$P < 0.05$
Kidney	I	904.1 ± 333.9	681.5 ± 86.3	392.3 ± 101.2	413.7 ± 45.7	416.2 ± 98.8	530.3 ± 86.7*	502.7 ± 118.5	773.9 ± 208.4 ^{**}	$P < 0.01$	$P < 0.05$
	II	702.6 ± 238.0	596.6 ± 140.6	417.7 ± 100.1	636.6 ± 238.8 ^a	464.5 ± 99.3	519.2 ± 158.3	597.7 ± 266.4	752.4 ± 201.2	N.S.	N.S.
Gills	I	386.1 ± 140.7	345.2 ± 93.6	470.3 ± 92.9	461.5 ± 74.1	404.4 ± 155.5	352.5 ± 157.6	401.7 ± 56.8	504.5 ± 195.4	N.S.	N.S.
	II	354.3 ± 50.3	413.3 ± 187.1	413.7 ± 150.8	410.3 ± 104.5	354.6 ± 93.6	357.0 ± 146.9	316.4 ± 103.0 ^a	208.0 ± 103.5 ^{ab}	N.S.	N.S.
Skin	I	234.6 ± 81.0	219.3 ± 26.0	209.6 ± 97.5	247.1 ± 113.6	365.3 ± 150.0	408.7 ± 207.4	439.5 ± 200.4	354.6 ± 160.6	$P < 0.05$	N.S.
	II	309.8 ± 62.9 ^a	316.0 ± 91.0 ^b	282.7 ± 60.9	419.6 ± 164.2 ^a	366.3 ± 81.8	461.1 ± 138.0	292.7 ± 115.6 ^a	270.6 ± 63.6	N.S.	N.S.
Muscles	I	105.5 ± 37.8	118.1 ± 40.5	86.7 ± 43.0	68.5 ± 33.1	104.7 ± 23.7	96.3 ± 10.7	113.7 ± 26.4	85.7 ± 13.9 ^{**}	N.S.	N.S.
	II	193.4 ± 93.2 ^b	159.6 ± 43.7	93.0 ± 28.9	93.6 ± 8.5	103.1 ± 28.5	117.3 ± 57.9	87.5 ± 24.1 ^a	116.9 ± 13.8 ^{**c}	$P < 0.05$	N.S.

Significant difference between the two sexes in the same site are represented by: *: $P < 0.05$; **: $P < 0.01$ and ***: $P < 0.001$

Significant difference between the two sites in the same sex are represented by: a: $P < 0.05$, b: $P < 0.01$ and c: $P < 0.001$

Numbers of samples in each site are represented in table 1

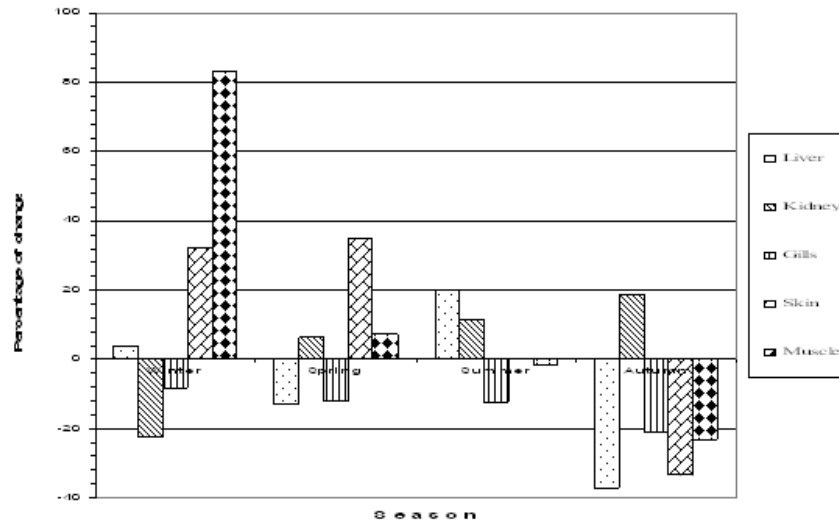


Fig. 2: The percentage of change in the iron concentrations in the liver, kidney, gills skin and muscles of male *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

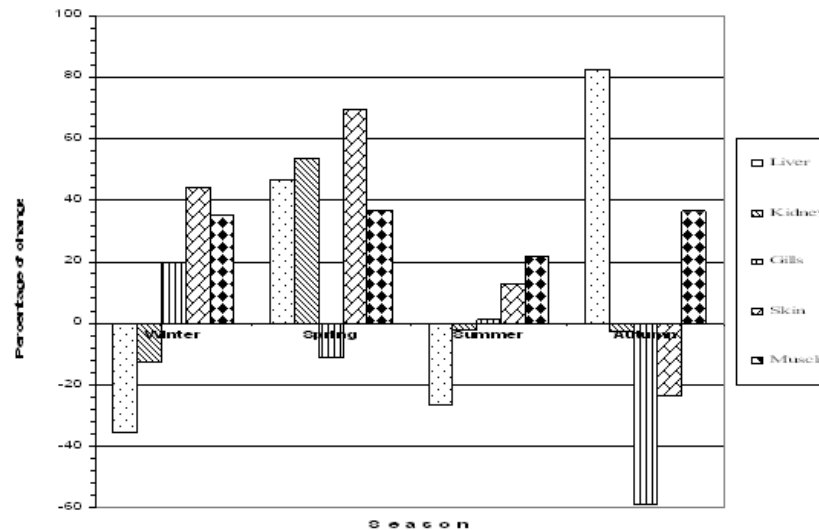


Fig. 3: The percentage of change in the iron concentrations in the liver, kidney, gills skin and muscles of female *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

Iron content in gills of both sexes at autumn season showed significant lower values in Barrage than Al-Aiat (21.2 and 58.8 % for ♂ and ♀ respectively). In skin, Fe content in both sexes at winter and female fish at spring showed significant higher values in Barrage area than Al-Aiat (32.1; 44.1 and 69.8 % respectively), while male fish at autumn recorded significant ($P < 0.05$) lower value (33.4 %). Iron content in muscles at winter showed significant ($P < 0.01$) higher value in male fish from Barrage than Al-Aiat (83.2 %). At autumn, significant lower (23.1 %) and higher (36.4 %) values were detected in males and females respectively between the two localities.

Copper (Table 4 and Figs. 4 & 5):

Comparison between the two areas showed that the liver copper of fish collected from Barrage area significantly differed than that from Al-Aiat area as follows: lower at winter for females (percentage of change: 61.5 %, Fig. 5) and at autumn for males

(44.8 %, Fig. 4) and higher values at summer for both sexes (64.7 and 103.4 % for ♂ and ♀ respectively). Both sexes from Barrage area recorded lower (37.4 and 48.4 % for ♂ and ♀ respectively) and higher (98.1 and 47.7 % for ♂ and ♀ respectively) significant values of Cu in the kidney at winter and summer respectively than that from Al-Aiat area. Gills Cu from both sexes at winter (93.0 and 122.7 % for ♂ and ♀ respectively); females at spring (31.9 %) and males at autumn (27.5 %) from Barrage area recorded significant higher values than that from Al-Aiat. The same significant higher values were demonstrated in the skin Cu from females at winter (367.5 %); both sexes at spring (903.8 and 518.2 % for ♂ and ♀ respectively) and males at autumn (229.5 %). Also, the significant higher values were detected in the muscles Cu from males at summer (103.3 %) and both sexes at autumn (40.0 and 50.3 % for ♂ and ♀ respectively).

Table 4: Mean ± standard deviation of copper concentration (µg g⁻¹ dry weight) in different tissues of both sexes of *Clarias gariepinus* collected from Al-Aiat (site I) and Barrage (site II) areas during the four seasons.

Tissue	Site	Winter		Spring		Summer		Autumn		ANOVA	
		Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Liver	I	226.0 ± 97.5	394.7 ± 110.3**	123.3 ± 79.6	230.9 ± 110.1*	165.8 ± 61.9	161.8 ± 70.7	257.5 ± 134.9	213.3 ± 107.0	N.S.	P < 0.05
	II	253.7 ± 167.2	152.2 ± 60.6 ^c	124.1 ± 49.9	153.7 ± 68.5	273.0 ± 34.7 ^c	328.9 ± 168.9 ^a	142.2 ± 74.2 ^a	284.8 ± 143.2 [*]	N.S.	N.S.
Kidney	I	67.631 ± 31.860	80.141 ± 12.491	29.639 ± 11.989	29.049 ± 8.986	38.269 ± 12.923	57.487 ± 14.429**	77.490 ± 30.615	98.709 ± 36.386	P < 0.05	P < 0.01
	II	42.345 ± 18.015 ^a	41.353 ± 16.059 ^c	30.741 ± 11.087	31.176 ± 12.472	75.789 ± 23.044 ^c	84.890 ± 21.660 ^b	85.011 ± 28.468	97.231 ± 45.248	P < 0.05	P < 0.01
Gills	I	19.465 ± 5.896	24.972 ± 7.165	27.010 ± 5.659	19.449 ± 4.097**	21.888 ± 7.912	19.178 ± 4.670	17.718 ± 4.023	27.489 ± 10.498**	N.S.	N.S.
	II	37.564 ± 13.495 ^c	55.604 ± 24.894 ^b	23.194 ± 11.554	25.659 ± 2.162 ^b	20.614 ± 2.925	19.909 ± 10.083	22.591 ± 4.736 ^a	22.706 ± 11.385	P < 0.05	P < 0.05
Skin	I	1.127 ± 0.550	0.428 ± 0.200**	0.577 ± 0.285	1.206 ± 0.663 [*]	4.933 ± 2.521	4.742 ± 2.252	2.454 ± 1.255	4.684 ± 2.339 [*]	P < 0.01	P < 0.01
	II	1.300 ± 0.697	2.001 ± 1.022 ^c	5.790 ± 2.483 ^c	7.458 ± 3.069 ^c	5.299 ± 2.662	7.777 ± 4.049	8.085 ± 4.161 ^c	7.605 ± 3.896	P < 0.05	P < 0.05
Muscles	I	2.831 ± 1.477	2.575 ± 1.103	2.541 ± 0.706	3.789 ± 1.404 [*]	4.250 ± 1.356	4.341 ± 1.395	6.577 ± 1.304	5.706 ± 1.745	P < 0.01	P < 0.05
	II	2.202 ± 1.140	1.890 ± 0.894	3.280 ± 1.266	3.135 ± 1.456	8.642 ± 4.364 ^b	5.798 ± 2.395	9.205 ± 2.559 ^b	8.577 ± 3.367 ^a	P < 0.01	P < 0.01

See footnote table 3

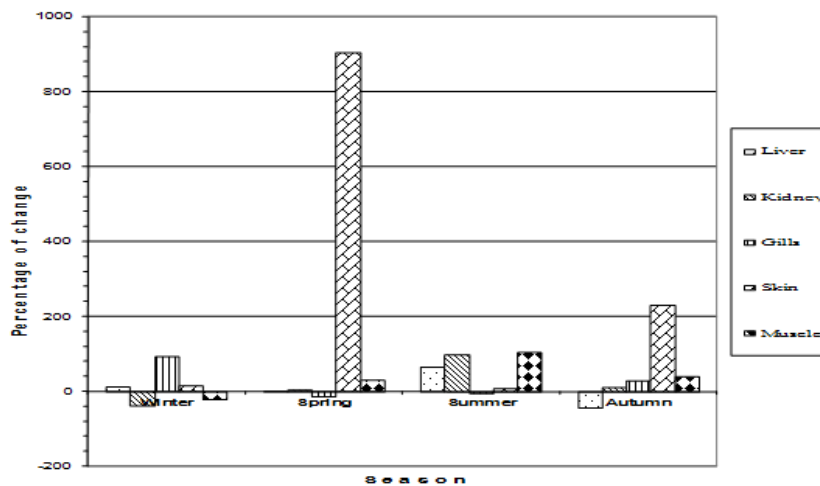


Fig. 4: The percentage of change in the copper concentrations in the liver, kidney, gills skin and muscles of male *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

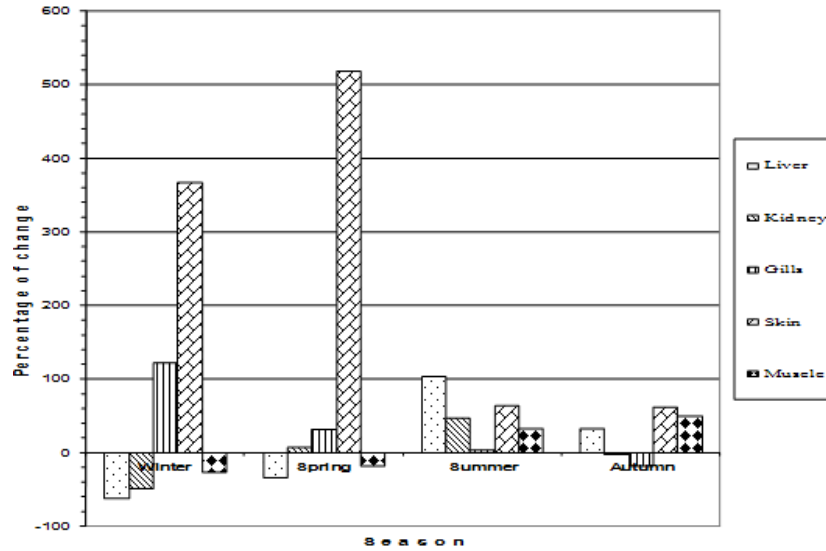


Fig. 5: The percentage of change in the copper concentrations in the liver, kidney, gills skin and muscles of female *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

Zinc (Table 5 and Figs. 6 & 7):

At winter, both sexes of fish collected from Barrage area recorded significant lower values (percentage change: 26.4 and 39.8 % for ♂ and ♀ respectively) of the liver Zn than that from Al-Aiat area. Contrary at summer, both sexes recorded significant higher values of Zn in both liver (58.4 and 66.6 % for ♂ and ♀ respectively) and skin (71.7 and 51.8 % for ♂ and ♀ respectively). Also, Zn in the gills of male fish recorded a significant higher value at autumn (24.7 %).

Table 5: Mean \pm standard deviation of zinc concentration ($\mu\text{g g}^{-1}$ dry weight) in different tissues of both sexes of *Clarias gariepinus* collected from Al-Aiat (site I) and Barrage (site II) areas during the four seasons.

Tissue	Site	Winter		Spring		Summer		Autumn		ANOVA	
		Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Liver	I	197.0 \pm 54.5	201.0 \pm 35.9	139.2 \pm 49.0	136.5 \pm 57.2	138.9 \pm 28.0	135.4 \pm 30.2	165.7 \pm 61.3	182.4 \pm 53.3	N.S.	N.S.
	II	144.9 \pm 33.8 ^a	121.0 \pm 61.8 ^b	115.7 \pm 21.3	125.6 \pm 28.5	220.1 \pm 68.5 ^b	225.5 \pm 71.6 ^b	175.4 \pm 44.2	199.9 \pm 41.2	P < 0.05	P < 0.05
Kidney	I	238.0 \pm 97.2	290.3 \pm 67.6	133.3 \pm 22.4	134.9 \pm 19.8	167.7 \pm 45.9	234.4 \pm 37.1 ^{**}	158.6 \pm 19.0	163.0 \pm 53.2	P < 0.05	P < 0.01
	II	226.9 \pm 48.4	245.3 \pm 67.7	141.3 \pm 22.4	144.0 \pm 24.9	174.0 \pm 35.6	260.0 \pm 128.1	171.4 \pm 46.0	147.5 \pm 37.9	P < 0.05	N.S.
Gills	I	74.786 \pm 5.350	72.434 \pm 6.972	72.056 \pm 9.220	72.756 \pm 7.345	80.173 \pm 18.442	77.456 \pm 9.617	65.425 \pm 15.604	76.726 \pm 32.236	N.S.	N.S.
	II	69.786 \pm 19.404	83.381 \pm 18.084	72.904 \pm 14.756	70.035 \pm 13.350	68.897 \pm 13.184	79.839 \pm 26.136	81.569 \pm 12.080 ^a	75.291 \pm 8.352	N.S.	N.S.
Skin	I	60.787 \pm 21.527	52.459 \pm 11.990	53.683 \pm 23.534	48.790 \pm 16.624	51.154 \pm 22.691	88.525 \pm 22.586 ^{**}	76.928 \pm 8.738	103.286 \pm 31.219 [*]	N.S.	P < 0.05
	II	41.246 \pm 23.562	42.901 \pm 18.151	41.718 \pm 11.726	51.586 \pm 17.299	87.846 \pm 41.681 ^a	134.417 \pm 10.704 ^{**c}	87.088 \pm 19.311	87.250 \pm 17.162	P < 0.05	P < 0.01
Muscles	I	26.681 \pm 11.100	30.688 \pm 8.732	27.487 \pm 10.106	34.473 \pm 17.288	40.532 \pm 7.837	25.367 \pm 12.866 ^{**}	27.557 \pm 13.452	26.184 \pm 13.455	N.S.	N.S.
	II	25.914 \pm 8.635	27.479 \pm 11.946	28.109 \pm 14.041	39.346 \pm 9.310	52.573 \pm 27.456	37.780 \pm 16.530	28.072 \pm 14.564	33.463 \pm 12.797	N.S.	N.S.

See footnote table 3

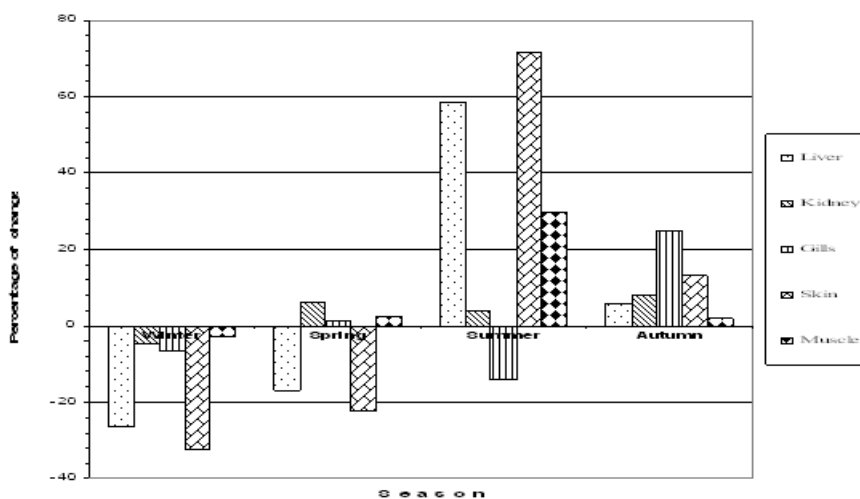


Fig. 6: The percentage of change in the zinc concentrations in the liver, kidney, gills skin and muscles of male *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

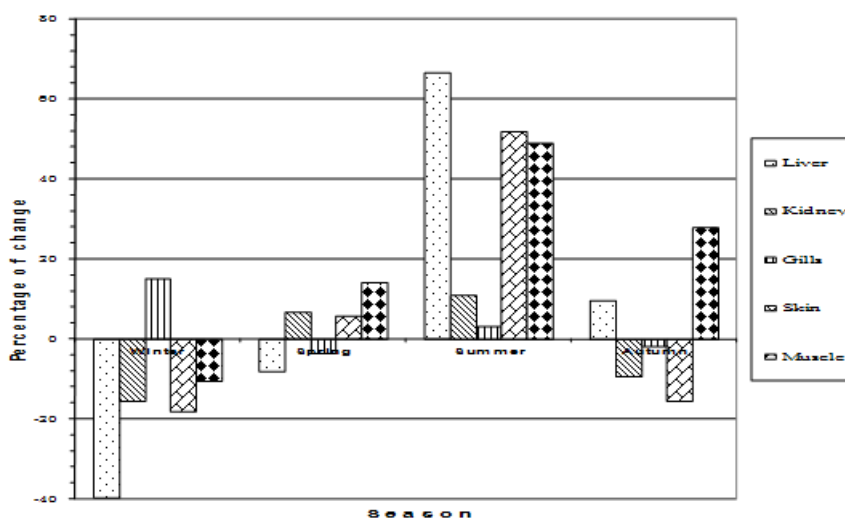


Fig. 7: The percentage of change in the zinc concentrations in the liver, kidney, gills skin and muscles of female *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

Manganese (Table 6 and Figs. 8 & 9):

At winter, both sexes of fish collected from Barrage area showed significant lower values of Mn in the kidney (percentage change: 38.8 and 31.3 % for ♂ and ♀ respectively); skin (42.1 and 34.4 % for ♂ and ♀ respectively) and muscles (60.3 and 57.5 % for ♂ and ♀ respectively) than that from Al-Aiat area. In the same season, females recorded a significant lower value of the liver Mn (36.5 %), while males showed significant higher values of Mn in both liver (80.6 %) and gills (107.6 %). At spring, the only significant lower value was detected in the gills of males (49.3 %) collected from Barrage area than that from Al-Aiat area. At summer, significant higher values of the Mn contents in the five organs of males (176.3, 64.1, 129.8, 71.0 and 53.6 % for liver, kidney, gills, skin and muscles respectively) and only in the gills of females (247.2 %) from Barrage area were demonstrated than that from Al-Aiat. At autumn, significant lower values of Mn were recorded in the kidney (57.8 and 62.1 %

for ♂ and ♀ respectively) and skin (55.6 and 60.1 % for ♂ and ♀ respectively) and in the muscles of female fish (49.1 %) collected from Barrage than Al-Aiat area.

Table 6: Mean \pm standard deviation of manganese concentration ($\mu\text{g g}^{-1}$ dry weight) in different tissues of both sexes of *Clarias gariepinus* collected from Al-Aiat (site I) and Barrage (site II) areas during the four seasons.

Tissue	Site	Winter		Spring		Summer		Autumn		ANOVA	
		Male	Female	Male	Female	Male	Female	Male	Female	Male	Female
Liver	I	1.528 \pm 0.923	3.567 \pm 0.569***	2.485 \pm 1.129	3.766 \pm 1.382	1.786 \pm 0.829	3.102 \pm 0.697**	4.301 \pm 1.570	4.612 \pm 0.947	P < 0.01	N.S.
	II	2.760 \pm 1.082 ^a	2.266 \pm 1.112 ^b	1.617 \pm 0.874	3.938 \pm 1.181***	4.936 \pm 2.523 ^c	4.350 \pm 2.251	4.383 \pm 1.896	5.104 \pm 1.110	P < 0.05	P < 0.05
Kidney	I	11.192 \pm 6.682	10.651 \pm 0.934	14.370 \pm 6.243	11.682 \pm 5.876	24.654 \pm 5.265	58.583 \pm 13.007***	53.269 \pm 18.097	53.101 \pm 22.778	P < 0.01	P < 0.01
	II	6.845 \pm 1.489 ^b	7.315 \pm 2.268 ^b	10.894 \pm 4.492	15.694 \pm 5.532	40.447 \pm 8.673 ^c	56.437 \pm 22.304	22.459 \pm 4.663 ^c	20.107 \pm 8.796 ^b	P < 0.01	P < 0.01
Gills	I	19.433 \pm 6.682	25.994 \pm 10.768	24.769 \pm 9.502	26.311 \pm 10.356	36.875 \pm 17.979	19.184 \pm 9.693 ^a	35.690 \pm 16.638	39.702 \pm 17.927	N.S.	N.S.
	II	40.338 \pm 13.435 ^c	27.848 \pm 12.303 ^b	12.548 \pm 4.180 ^b	37.285 \pm 15.410***	84.728 \pm 29.739 ^c	66.600 \pm 15.918 ^c	33.375 \pm 14.710	36.640 \pm 7.424	P < 0.01	P < 0.01
Skin	I	9.116 \pm 4.241	8.593 \pm 0.986	11.170 \pm 4.893	9.099 \pm 4.765	18.229 \pm 5.160	50.651 \pm 21.727***	38.950 \pm 16.438	38.820 \pm 19.038	P < 0.01	P < 0.01
	II	5.275 \pm 1.147 ^a	5.637 \pm 1.748 ^c	8.395 \pm 3.462	12.094 \pm 4.263	31.170 \pm 6.683 ^c	43.492 \pm 17.188	17.308 \pm 3.594 ^c	15.496 \pm 6.779 ^b	P < 0.01	P < 0.01
Muscles	I	5.775 \pm 2.671	5.049 \pm 2.617	2.846 \pm 0.601	3.797 \pm 1.754	3.608 \pm 1.305	3.983 \pm 1.624	1.991 \pm 0.840	2.280 \pm 0.527	P < 0.05	N.S.
	II	2.295 \pm 1.122 ^b	2.147 \pm 1.301 ^b	3.452 \pm 1.048	2.961 \pm 1.124	5.540 \pm 1.135 ^b	3.097 \pm 1.278***	1.545 \pm 0.720	1.161 \pm 0.284 ^c	P < 0.01	N.S.

See footnote table 3

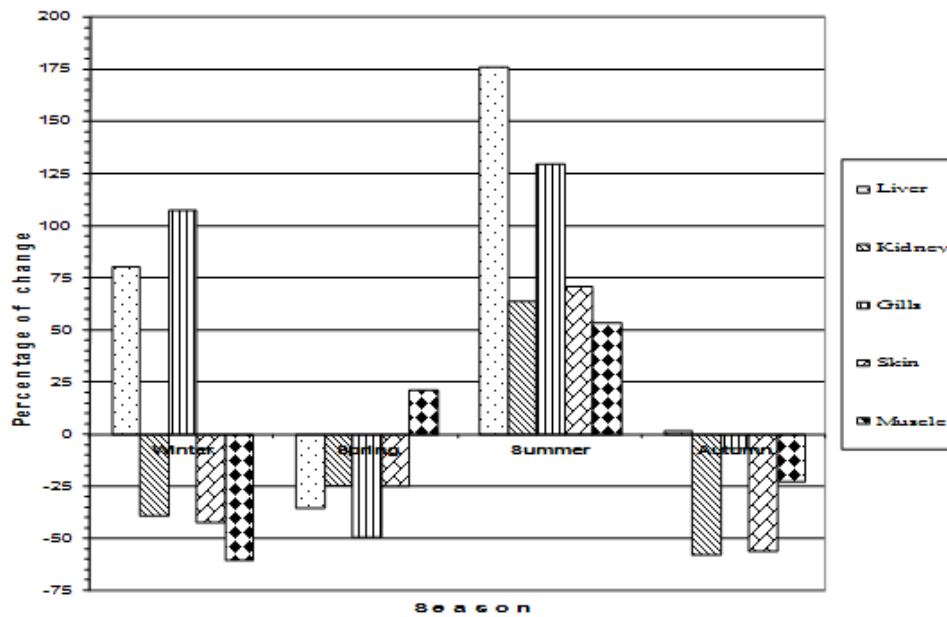


Fig. 8: The percentage of change in the manganese concentrations in the liver, kidney, gills skin and muscles of male *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

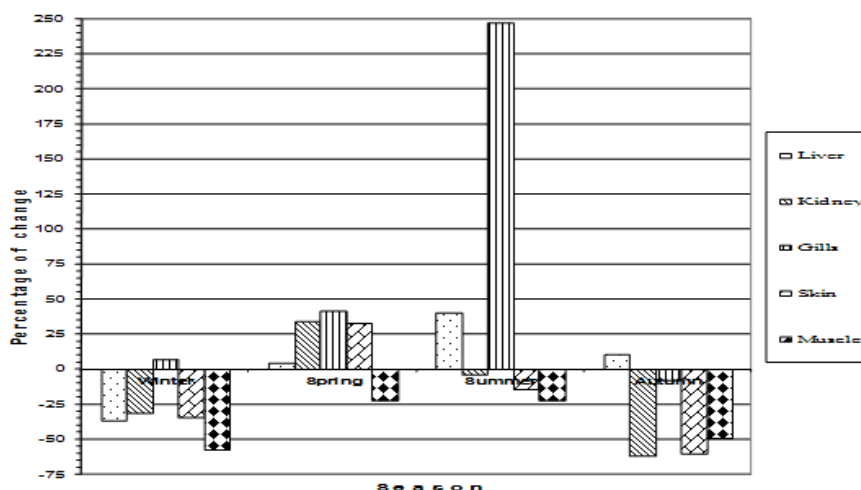


Fig. 9: The percentage of change in the manganese concentrations in the liver, kidney, gills skin and muscles of female *Clarias gariepinus* from Barrage (site II) relative to Al-Aiat (site I) during the four seasons.

2) Effect of sex:

Iron (Table 3):

At winter, only liver Fe in female fish from Al-Aiat region had a significant ($P < 0.05$) higher value than male ones. At spring, females from Barrage area had significant ($P < 0.05$) higher values of the kidney and skin Fe than males. At summer, kidney Fe was the only value that significantly ($P < 0.05$) higher in female fish from Al-Aiat area than male ones. At autumn, significant lower values of Fe in both liver ($P < 0.05$) and muscles ($P < 0.01$) and significant higher value in the kidney ($P < 0.01$) of females from Al-Aiat area were demonstrated compared to the males. Fish collected from Barrage area showed significant higher values of Fe in both liver ($P < 0.05$) and muscles ($P < 0.01$) and significant lower values in the gills ($P < 0.05$) than males.

Copper (Table 4):

Female fish collected from Al-Aiat region demonstrated significant Cu values compared to males as follows: higher values in the liver at winter ($P < 0.01$) and spring ($P < 0.05$); higher value ($P < 0.01$) in the kidney at summer; lower and higher values ($P < 0.01$) in the gills at spring and autumn respectively; lower value ($P < 0.01$) in the skin at winter and higher values ($P < 0.05$) at both spring and autumn; and higher value ($P < 0.05$) in the muscles at spring. The only significant ($P < 0.05$) higher value in female fish from Barrage area was detected in the liver at autumn than males.

Zinc (Table 5):

At summer, female fish showed significant ($P < 0.01$) higher values of Zn in the kidney (from Al-Aiat) and skin (from both areas) and lower value in the muscles (from Al-Aiat) than the respective males. At autumn, the only significant ($P < 0.05$) value was detected in the skin of female fish from Al-Aiat area that showed higher value than male.

Manganese (Table 6):

Female fish from Al-Aiat area demonstrated the following significant values of Mn compared to the males: higher values in the liver at both winter ($P < 0.001$) and summer ($P < 0.01$); higher values ($P < 0.001$) in both kidney and skin at summer; and lower value ($P < 0.05$) in the gills at summer. Female fish from Barrage area represent the following: higher values ($P < 0.001$) in both liver and gills at spring; lower value ($P < 0.05$) in the gills at winter; and lower value ($P < 0.001$) in the muscles at summer.

3) Effect of season:

Iron (Table 3):

Almost the maximum and minimum values of the iron in the five organs were recorded at winter and spring respectively. The maximum values were detected as follows: for liver in both sexes from Al-Aiat and males from Barrage; for muscles in both sexes from Barrage and females from Al-Aiat; and for kidney in males from both locations. Another peak of the liver Fe was observed at autumn in male fish from Al-Aiat. The minimum values were observed as follows: for liver and muscles in both sexes from both areas; for kidney in both sexes from Al-Aiat and males from Barrage; and for skin in males from both locations. Another lower value of the muscles Fe was shown in male fish from Barrage at autumn. The maximum and minimum values of Fe in the gills of both sexes from Barrage were detected at spring and autumn respectively. The maximum values of Fe in the skin were found at summer for both sexes from both locations. Females from both areas recorded maximum values of Fe in the kidney at autumn. The minimum values of Fe in the gills of both sexes from Al-Aiat were found at winter. The other maximum and minimum values were illustrated in table 3. ANOVA analysis demonstrated that season significantly affects on the Fe concentrations as follows: in the liver of both sexes from the two localities; in the kidney of both sexes from Al-Aiat; and in the skin and muscles of males from Al-Aiat and Barrage areas respectively.

Copper (Table 4):

Copper concentrations in the kidney of all fish groups showed the maximum and minimum values at autumn and spring respectively. Also the maximum values of Cu in the muscles of the four groups were recorded at autumn but the minimum values were at winter except males from Al-Aiat at spring. Both sexes from Barrage showed maximum and minimum values of Cu in the liver at summer and spring respectively, but another lower value was observed at winter for females. The Cu values in the gills of both sexes from Barrage were highest and lowest at winter and summer respectively. Both sexes from Al-Aiat and females from Barrage recorded the maximum values of Cu in the skin at summer, while both sexes from Barrage and females from Al-Aiat recorded the minimum values at winter. The other maximum and minimum values were demonstrated in table 4. Copper contents in the kidney, skin and muscles of both sexes from both locations were significantly affected by season. Also ANOVA showed that gill's Cu in both sexes from Barrage and liver's Cu in females from Al-Aiat were significantly ($P < 0.05$) affected by season.

Zinc (Table 5):

The maximum concentrations of Zn in the liver of both sexes from Al-Aiat and Barrage were detected at winter and summer respectively, while the minimum values for all were recorded at spring except the female fish from barrage at winter. For Zn in the kidney, the minimum values for all groups were observed at spring, while the maximum values were demonstrated at winter except the female fish from barrage at summer. For Zn in the gills, higher values for both sexes from Al-Aiat were detected at summer and the lower values at autumn and winter for males and females respectively. Fish from Barrage did not show a typical pattern for both sexes. For Zn in the skin, the maximum values in both sexes from Al-Aiat and Barrage were shown at autumn and summer respectively, while the minimum values in both sexes from Barrage were detected at winter. For Zn in the muscles, the maximum values in males and females from both areas were recorded at summer and spring respectively, while the minimum values for both sexes from Barrage were detected at winter. The other values were illustrated in table 5. ANOVA demonstrated that Zn concentration in the

liver and skin (Barrage); kidney (Al-Aiat) of both sexes; kidney (Barrage) of males; and skin (Al-Aiat) of females were affected by season.

Manganese (Table 6):

An obvious similarity was observed between the concentrations of Mn in both kidney and skin of both sexes from both areas. The minimum values were recorded at winter for all groups, while the maximum values were detected at summer except males from Al-Aiat at autumn. Another similarity was illustrated between Mn contents in both liver and gills. The minimum values were at winter for males (Al-Aiat) and females (Barrage); at spring for males (Barrage); and at summer for females (Al-Aiat). The maximum values of liver's Mn were at autumn for all groups except males from Barrage at summer, contrary values of gill's Mn were at summer except females from Al-Aiat at autumn. The Mn contents in the muscles demonstrated maximum values at winter and summer for both sexes from Al-Aiat and Barrage respectively, while the minimum values were at autumn for all groups. Manganese contents in the kidney and skin (both sexes from both areas); in the liver and gills (both sexes from Barrage); in the liver (males from Al-Aiat); and in the muscles (males from both areas) were affected by season as analyzed by ANOVA test.

4) Ranking of heavy metals in organs:

Tables 7 and 8 illustrate the distribution of the four elements in the five organs of both sexes in both localities. Iron and copper are similar in their distributions in both sexes, in which liver is the main site of accumulation followed by the kidney then gills. Muscles are the last organ that accumulates Fe in both sexes, while skin is the last organ that accumulate Cu in males and equal to the muscles in females. Kidney and gills in both sexes are the main organs that accumulate Zn and Mn respectively. For Zn, liver is the second organ followed by the gills and lastly the muscles. Skin is equal to the gills for Zn accumulation in case of females. For Mn, kidney is the second organ followed by the skin and lastly the liver (males) or muscles (females).

Table 7: Ranking of iron, copper, zinc and manganese distribution in different organs of male *Clarias gariepinus* collected from Al-Aiat and Barrage areas all over the year.

Metal	Liver	Kidney	Gills	Skin	Muscle
Fe	1	2	3	4	5
Cu	1	2	3	5	4
Zn	2	1	3	4	5
Mn	5	2	1	3	4

Table 8: Ranking of iron, copper, zinc and manganese distribution in different organs of female *Clarias gariepinus* collected from Al-Aiat and Barrage areas all over the year.

Metal	Liver	Kidney	Gills	Skin	Muscle
Fe	1	2	3	4	5
Cu	1	2	3	4	4
Zn	2	1	3	3	4
Mn	4	2	1	3	5

DISCUSSION

All over the year, the present water Fe levels in both Al-Aiat and Barrage areas (table 2) are much lower than that recorded by Issa *et al.* (1997) in both Helwan (8.84-10.54 mg l⁻¹) and Barrage (0.364 mg l⁻¹). Khalaf-Allah (1998) reported that the mean value of Fe concentration in water samples around Helwan exceeded the permissible limits set by WHO (1984). Contrary to Issa *et al.* (1997) who mentioned that the Fe

content in the Nile water is slightly affected by water temperature, the present data did not reveal any seasonal variation (table 2). El-Nady (1981) and Issa *et al.* (1997) noted that there is a negative correlation between dissolved heavy metals and dissolved oxygen. It is known that ferrous (which is believed to be toxic) and ferric salts are usually soluble in areas poor in dissolved oxygen (Hem, 1989). Wetzel (1983) and Hem (1989) stated that the occurrence of Fe in water strongly influenced by the presence of organic wastes and plant debris in soil. On the other hand, Rizkalla and Abo-Donia (1996_a) found that phytoplankton evidently was one of the factors causing the removal of the Fe from water.

Water copper levels in Barrage area at both winter and autumn are significantly lower than that in Al-Aiat area (table 2). The Cu levels in both areas are much lower than that recorded by Issa *et al.* (1997) in Helwan and Barrage areas (4.63-30.57 mg l⁻¹). Working on the River Nile water around Helwan, Khalaf-Allah (1998) reported that the mean value of Cu concentrations were within the guide line values of WHO (1984). This lower value was confirmed by Daoud *et al.* (1999) on the Cu and Zn concentrations in water from Helwan. The calculated global averages for river water were presented by Liebman (1960) to be 7 µg /l. Alabaster and Lloyd (1980) recorded that the natural concentrations of Cu in water are at <5 µg/l, but according to the Department of Water Affairs and Forestry (1993_b) levels of 12 mg/l have been recorded in South Africa. The aqueous Cu exposure studies on *O. niloticus* confirm that Cu can be acutely toxic at around 1–5 µg l⁻¹ total Cu (Coğun and Kargin, 2004). According to Stiff (1971), the soluble forms of Cu are the only forms available to fish. The toxicity of Cu appears to be related to the soluble form, with Cu²⁺ and, to some extent, the Cu hydroxyl ion being the toxic forms. The free ion rarely occurs in aquatic environments as the soluble form of Cu in river waters and consists mainly of complexed, non-toxic forms. Lloyd (1992) found that the main environmental factor that affects copper toxicity in water is calcium concentration. This is as a result of the competition that occurs between these two ions for binding sites in the tissue of the gills and other organs. Copper in the alkaline conditions precipitates as the carbonate and is non toxic (Dallas and Day, 1993). Humic acids, hardness, temperature, pH, dissolved oxygen and suspended solids can have a significant altering effect on the bioavailability of Cu to fish (Stiff, 1971; Moore and Ramamoorthy, 1984). The results of Issa *et al.* (1997) indicated that Cu is negatively correlated with water transparency and dissolved oxygen as a result of the formation of insoluble CuO and is positively correlated with total dissolved substances.

The records of Issa *et al.* (1997) on Zn distribution in River Nile showed two peaks in the surface water at Helwan (375.7 mg l⁻¹) during summer and 299.77 mg l⁻¹ at Barrage during spring and the minimum value (20.76 mg l⁻¹) is shown at Helwan during spring season. These data are much higher than that recorded in the present study (table 2). The calculated global averages for river water were presented by Liebman (1960) to be 20 µg/l. Issa *et al.* (1997) related the highly significant positive correlation between Zn and suspended matter to adsorption of zinc with anhydrous Fe₂O₃ and Al₂O₃ which acts as scavenger for zinc. On the other hand, the highly significant negative correlation between Zn and dissolved oxygen is attributed to the increase of the precipitation of zinc as Zn (OH)₂ at high pH in the presence of oxygen. Hassel *et al.* (1980) found that concentrations of Zn was low in stream water samples obtained at sites adjacent to highways and stream sediments appeared to serve as the strong reservoir and primary source for bioaccumulation of heavy metals.

No significant difference in the concentrations of manganese in the water of River Nile between Al-Aiat and Barrage areas were observed except at summer (table

2). The lowest concentration of Mn during summer in Barrage area may be attributed to uptake of Mn by phytoplankton in which the dead phytoplankton is settled to the sediment leaving the water poor in the trace metal (Issa *et al.*, 1997). They reported that Mn shows the highest concentration at Helwan (552.76 mg l⁻¹) in winter season and the lower of (17.14 mg l⁻¹) during summer. Barlas (1999) found that concentration of water Cu and Mn differed by seasons. Rizkalla and Abo-Donia (1996_a) reported that Fe and Mn in River Nile water of Upper Egypt indicated significant variations with region. Issa *et al.* (1997) said that Mn is: slightly correlated with temperature; negatively correlated with dissolved oxygen (due to oxidation of Mn and uptake of it by the phytoplankton); and highly significant positive correlated with total suspended substances (due to the adsorption of Mn on the surface of suspended sediments). The toxicity of manganese is not dependent on the total manganese concentration, but the concentration of oxidized manganese which is available (Clement Associates, 1985). Higher concentrations of Ca²⁺ ions will compete with Mn ions for absorption through the gill surface thus decreasing the bioavailability of manganese to fish (Seymore *et al.*, 1995).

Rizkalla and Abo Donia (1996_{a,b}) and Daoud *et al.* (1999) pointed to the idea that the concentrations of heavy metals in the aquatic environment can be correlated to their concentrations in the bodies of animals surviving in such environment. The exchange processes between the metallic trace elements of water and the fish that live therein is dependent upon factors influenced by the environment and upon biological factors (Harms, 1975). Fast *et al.* (1990) indicated in their experiment that metal uptake from the water was not of significant concern and the principal source of heavy metals in salmon was from diet. Rizkalla and Abo Donia (1996_a) computed that deboned flesh concentrations of Fe and Mn in *Oreochromis niloticus* were bioaccumulated from water, and Zn from sediment. Gaber (2008) revealed significant positive correlations between heavy metals concentrations in tilapia flesh and water.

Significant variation among individuals was observed for all bioaccumulated metals tested and in all the organs sampled. Also, concentration differences were observed for the individual metals in the same organs. The differences in tissue metal concentrations of fish from a specific locality were cited by Du Preez and Steyn (1992). The present results revealed that liver is the main organ of iron accumulation in both sexes of *C. gariepinus* and the maximum and minimum concentrations occurred in winter and spring respectively (table 3). Avenant-Oldewage and Marx (2000) concluded the same observation on the same fish species. The liver has a vast vascular network where blood passes through. Iron released from the breakdown of haemoglobin, as well as excess Fe found in the body, is stored and detoxified in the liver (Buckley *et al.*, 1982). Kidney is the 2nd organ that accumulates Fe (table 3). Rizkalla *et al.* (2003) illustrated that kidney, spleen and liver are the main sites of Fe deposition. Gills are the 3rd organ that accumulates Fe, and the maximum concentrations were recorded at spring while the minimum concentrations were at winter and autumn for fish collected from Al-Aiat and Barrage respectively (table 3). Avenant-Oldewage and Marx (2000) said that the high concentrations of Fe found in the sediment could have resulted in the high Fe levels in the gills during the process of bottom feeding of *C. gariepinus*. Laurent and Dunel (1980) mentioned that with an immense vascular network in close proximity to the gill tissue, the gills will be in continual contact with the blood-borne Fe. Finally, the minimal concentrations of Fe were detected in muscles (table 3). Working on *C. gariepinus*, Avenant-Oldewage and Marx (2000) reported that the low storage of iron in muscle would be accompanied by low iron concentrations in the skin and no significant difference were found between

them. On the other hand, Adeyeye *et al.* (1996) and Olaifa *et al.* (2004_b) observed that Fe is the dominant metal in the muscle of *C. gariepinus*. Some scattered significant differences in the concentrations of Fe in different organs (especially skin) between Al-Aiat and Barrage areas were detected (table 3). Rizkalla and Abo Donia (1996_a) referred that after Zn, Fe is the most common metallic trace element in deboned flesh of *Oreochromis niloticus* and their data supported the impression that metal-specific differences in the concentration levels existed between different localities. The significant seasonal variations in the Fe concentrations were obviously detected in the liver of both sexes from both localities (table 3). Avenant-Oldewage and Marx (2000) showed seasonal changes in the concentration of Fe in the liver of *C. gariepinus* as well as in the skin and muscle. As previously mentioned, increasing water temperatures enhance the oxidation of the soluble Fe²⁺ to the insoluble Fe³⁺ iron states. The abiotic factors mentioned above are also at a maximum level during winter (Department of Water Affairs and Forestry, 1993_a).

As iron, the major site for the accumulation of copper is the liver (table 4). Hogstrand *et al.* (1991) and Carvalho *et al.* (2004_a) demonstrated high copper accumulation in the livers of *Perca fluviatilis* and *Prochilodus scrofa* with concomitant expression of metallothioneins (MT) in the liver. However, it reinforces the view that the liver in fish plays a protective role against chronic heavy metal exposures by producing MT (Carpene and Vařák, 1989), acting as a storage site, and being a vital organ in the detoxification mechanisms of copper (Buckley *et al.*, 1982 and Mayer *et al.*, 2003). Kidney is the 2nd organ that accumulates Cu and the maximum and minimum concentrations were at autumn and spring respectively (table 4). The highest copper concentration in the kidney of *Clarias gariepinus* (Farombi *et al.*, 2007) may be due to the fact that fish kidney contains a cystine rich copper binding protein which is thought to have either a detoxifying or storage function as reported by Luckey and Venugopal (1977). Gills are the 3rd organ that accumulates Cu (table 4). *Clarias* do not store significant higher levels of Cu in their gills, but *Tilapia* species showed significant higher concentrations of this metal in their gills (El-Shehawi *et al.*, 2007). Shaw and Handy (2006) showed that Nile *Tilapia* fish accumulate excess Cu in the liver and gills. DeOliveira *et al.* (2004) reported that Cu²⁺ accumulated in tambaqui (*Colossoma macropomum*), in decreasing order, gills > liver. Several authors (Gatlin *et al.*, 1989 and Miller *et al.*, 1993) have shown that increased concentrations in the liver and gills were due to increased Cu in the diet. The gill tissue of the fish tends to concentrate Cu from the water either due to the gills possesses an extensive vascular network as previously mentioned by Laurent and Dunel (1980) or due to the short diffusion distance from the water to the blood, as well as the large surface area exposed to the water (Stagg and Shuttleworth, 1982). It has been concluded from the results of many studies that the accumulation of Cu in the gill is possibly due to its binding to haemopoietic tissue, mucous and metallothioneins implicated with excretion and detoxification (Avenant-Oldewage and Marx, 2000). The lowest concentrations of Cu were recorded in the muscles with the maximum and minimum values at autumn and winter respectively (table 4). Higher Cu values were estimated by Seddek *et al.* (1996) in *C. lazera* muscles (5.55 ppm), but lower values 0.03 ± 0.004 ppm were recorded by Abd El-Khalek *et al.* (2002). Abd El-Nasser *et al.* (1996) revealed an elevation of Cu in *Oreochromis niloticus* muscle in comparison to *C. lazera*. These findings contradict that of Hassan and Youssef (1985) who reported that Cu concentration in muscles of *C. lazera* was higher than that of *Tilapia*, while little difference was found by Ghazaly *et al.* (1992) and Rizkalla *et al.* (2003) between the metal content of the two species. According to

Moore and Ramamoorthy (1984), fish muscle normally contains low concentrations of Cu and, even at high levels of Cu exposure; muscle does not often reflect increases in the external environment. Contrary to Fe, Cu concentrations in different organs recorded large numbers of significant values between Al-Aiat and Barrage areas, while significant sex variation was fewer (table 4). Ghazaly *et al.* (1992) and Rizkalla *et al.* (2003) found that Cu level in the muscles of *C. lazera* and *O. niloticus* was affected by the locality and Cu concentration in gills from three different localities had a small range of variation. Significant difference in the concentrations of Cu in the muscles of both sexes of *Sardinella aurita* was reported by Shakweer and Abbas (1996). An obvious significant seasonal effect was demonstrated in the concentrations of Cu in the kidney, skin and muscles (table 4). The higher the temperature, the more ionized copper forms are produced resulting in greater toxicity to the fish (Prosi, 1979). The seasonal pattern observed by Avenant-Oldewage and Marx (2000) showed that in winter bioaccumulation was at a minimum, while generally in summer bioaccumulation rates were at a maximum. The effect of temperature seems to be evident in the MT concentration (Carvalho *et al.*, 2004_{a,b}).

The main storing site of zinc in both sexes of *C. gariepinus* collected from Al-Aiat and Barrage areas is the kidney followed by the liver (tables 5, 7 & 8). The high accumulation of Zn in the kidney could be based on specific metabolism process and co-enzyme catalyzed reactions involving Zn taking place in the kidney (Jaffar and Pervaiz, 1989). Zn also acts as a catalyst in metal biomolecules bound to amino acid side chains containing N, O and/or sulphur legends (Kendrick *et al.*, 1992) to form tetrahedral zinc metalloproteins and metalloenzymes in kidney tissues (Ashraf, 2005). High concentration of Zn was reported in the liver of seven fish species from the coastal waters of Uruguay (Viana *et al.*, 2005). Also, Annune and Iyaniwura (1993) reported the liver of *Oreochromis niloticus* and *Clarias gariepinus* to have accumulated Zn more than other tissues. Moreover, Farombi *et al.* (2007) observed high accumulation of Zn in the liver and gills of *C. gariepinus*. The high level of Zn in the liver may possibly reflect the multifunctional role of the liver in the detoxification (through metallothioneins binding) and storage processes (Carpene *et al.*, 1990). Gills are the 3rd organ that accumulates Zn, but in the female fish skin takes the same level (tables 7 & 8). Annune and Iyaniwura (1993) and Gbem *et al.* (2001) studied the bioaccumulation of trace metals in the gills of several fish species including *C. gariepinus*. The highest accumulation of Zn in the gills may be due to the facts that gills are in direct contact with the contaminated water; have the thinnest epithelium of all the organs; metals can penetrate through the thin epithelial cells (active process) and serves as the respiratory organ through which metal ions are absorbed (Bebianno *et al.*, 2004). The present results agreed with Badsha and Goldspink (1982); Annune and Iyaniwura (1993); Gbem *et al.* (2001) and Birungi *et al.* (2007) that the lowest Zn loads were found in the muscles. The Zn concentration in *C. lazera* dry muscle recorded by Abd El-Khalek *et al.* (2002) was 0.27 ± 0.03 ppm. This might be attributed to the growth factor as growth may dilute toxicant concentration if growth is faster than accumulation (Badsha and Goldspink, 1982). Jeng and Sun (1981) fed high levels of Zn sulfate to *Cyprinus carpio* and found Zn levels to be higher in the skeletal tissues, and that muscle metal levels were not increased till skeletal tissues are saturated. No clear sex differences were recorded (table 5). Shakweer and Abbas (1996) found that the differences between Zn concentrations in the muscles of the males and females of *Oreochromis niloticus* and *Sardinella aurita* were not significant while its concentration in the liver of the females of *Sardinella aurita* differed significantly from the corresponding concentrations in the males.

The highest values of manganese were recorded in the gills of both sexes of *C. gariepinus* from both sites studied (table 6). This result was confirmed by the results of Abdel-Baky (2001) on the same fish species. The mean Mn concentration in gills of *C. gariepinus* was 0.014 ppm in the dry season and 0.063 ppm in the wet season (Olaifa *et al.*, 2004_b). Also, working on 230 fish from the Rockall Trough (North-Eastern Atlantic), Vas *et al.* (1993) found that Mn accumulated mainly in gill tissues. The high accumulation of Mn in gill tissues may be attributed to the complex formation between metal ion and the protein structure in gills which contain nitrogen, oxygen and/or sulfur as reported by Cotton and Wilkinson (1980). Liver and muscles showed the least organs that accumulate Mn (tables 6 – 8). Olaifa *et al.* (2004_b) recorded higher concentrations of manganese in muscle tissue of *C. gariepinus* (2.17 ppm in the dry season and 0.315 ppm in wet season). Among the metals, Mn was lowest in the muscle of mullet (*Liza abu*) and catfish (*Silurus triostegus*) from the Atatürk Dam Lake, Turkey (Karadede *et al.*, 2004). Significant location and seasonal variations were recorded in the Mn concentration in different organs with maximum and minimum values at summer and winter respectively (table 6). No significant variation was recorded by Olaifa *et al.* (2004_b) between stations and seasons in Mn concentrations in muscles of *C. gariepinus*. Also but to a least extend, significant sex variation was detected (table 6). Shakweer and Abbas (1996) observed that the flesh of the males of *Sardinella aurita* contained significantly higher concentrations of Mn than that in the females.

Wepener *et al.* (2001) said that gill tissue is the initial site of accumulation of water-borne metals. Although the fish were exposed to a metal mixture, the interactions between metals and the external gill surface, as well as the subsequent uptake rate, were associated with the particular chemical properties of individual metals. The tendency of the individual metals in the metal mixture to bind to the external gill surface via ionic bonds, and to gill cytosolic compounds via covalent bonds, was $Cu > Fe > Zn$. Roméo *et al.* (2005) found that gills presented the highest Cu and Zn concentrations compared to the visceral mass or the remaining tissues. The gills and the liver are more often recommended as environmental indicator organs of water pollution than any other fish organs (Al-Yousuf *et al.*, 2000; Arain *et al.*, 2008). These two tissues have the highest metal burdens and represent the bioavailability of metal concentrations in the environment. The gills are directly in contact with water. Thus, the concentrations of metals in the gills reflect the concentrations of metals in the waters, whereas the concentrations in liver represent storage of metals (Rao and Padmaja, 2000). In general, Birungi *et al.* (2007) concluded that the order of accumulation of metals in tissue of *Oreochromis niloticus* was $Cu > Zn > Mn$ and $gills > liver > muscle$.

The effect of locality on metal concentrations in teleosts was highly significant as recorded by Walker (1982). Niazy *et al.* (1995) revealed significant variations in the concentrations of Cu, Fe and Zn in both livers and muscles of *Clarias lazera* trapped from different localities in Egypt and the data collected by Rizkalla and Abo Donia (1996_a) supported the impression that significant metal-specific differences in the concentration levels of Cu, Fe, Mn and Zn in muscle tilapia fish existed between the different localities from the upper section of the River Nile. Also, intra-location differences were detected in *C. gariepinus* for Zn and Mn concentrations in the gills; Cu and Zn concentrations in the muscles (Olaifa *et al.*, 2004_b) and Cu, Zn and Mn in the muscles, liver and kidney (Abdel-Baky, 2001). Chernoff and Dooley (1979) reported significant differences between males and females with respect to whole-body Zn and Cu concentrations, but no sex difference for Mn. Also, Rizkalla *et al.*

(2003) declared significant variation between male and female fishes from Mariut Lake and Mn is the least heavy metal shows sexual difference. Saleh *et al.* (1988) mentioned that Cu and Zn concentrations in *Tilapia zillii* from Wadi El-raiyan Lakes did not change significantly with the season of collection, while *Oreochromis niloticus* tissues showed seasonal variations in the concentrations of Fe, Zn and Cu. Also, Olaifa *et al.* (2004_b) reported significant seasonal differences in the concentrations of Cu and Zn in the gills of *C. gariepinus* and Cu and Fe in the muscles. The increased accumulation of heavy metals in fish tissues during winter and autumn might be due to the intensive feeding on phytoplankton and other organisms during these seasons (Saleh *et al.*, 1988; Al-Nagaaway *et al.*, 2009).

Working on *C. gariepinus*, metal accumulation was in the order of: Zn > Cu > Mn (Abdel-Baky, 2001 and Farombi *et al.*, 2007) or Cu > Zn (Gbem *et al.*, 2001). These orders of accumulation may be due to the permeability of *C. gariepinus* to these metals. There could be competition for protein-binding sites both at the mucosal cell level and in tissues. Possible mechanisms of metal-metal interaction include interchange of metal bound proteins; induction of metal-binding protein; and formation of compound complexes among metals and metalloids (Gbem *et al.*, 2001).

All five tissue types tested in the present work reflected differences when compared to each other, indicating a high degree of variability between these tissue types. Ranking of the different metals studied in the five organs (tables 7 & 8) demonstrated that Fe was detected in all tissues sampled and *C. gariepinus* is able to bioaccumulate high levels of Fe. Previous literature existed great variations in the levels of Fe concentrations in the different tissues either liver > gills > muscle > skin (Avenant-Oldewage and Marx, 2000) or kidney > liver > gills > skin > muscles (Rizkalla *et al.*, 2003). For Cu, differences in the Cu concentrations in the different organs of *C. gariepinus* were existed between the present study and other workers. The concentration in tissues was found to be in the following sequence: liver > gills > muscle > skin (Avenant-Oldewage and Marx, 2000); liver > gills > skin > muscle (Gbem *et al.*, 2001); liver > kidney > gills > muscles (Abdel-Baky, 2001) or kidney > liver > gills (Farombi *et al.*, 2007). The livers of *Oreochromis niloticus* and *Sardinella aurita* (Shakweer and Abbas, 1996) and some fish species from Lake Mariut and Nozha Hydrodrome (Shakweer and Abbas, 1997) accumulate high concentrations of Cu if compared by its concentrations in the flesh or gonads. In the same trend, Rizkalla *et al.* (2003) reported that the highest and lowest concentrations of Cu are shown respectively in the liver and muscles of *Oreochromis niloticus*; *C. gariepinus* and *Bagrus bayad*. Also Buckley *et al.* (1982); Du Preez and Steyn (1992); and Vas *et al.* (1993) indicated that, in fish, Cu appeared to selectively accumulate in liver tissue and muscle tissue was a poor indicator of increased metal availability. In contrast, elevated concentrations of Cu were noted by Ghazaly *et al.* (1992) in the gills and trace amounts were accumulated in muscles of some commercial fishes from Alexandria. The relative accumulation of Cu in tissue of *Oreochromis niloticus* was of the order gills > liver > muscle (Birungi *et al.*, 2007). Certain physiological processes may be stimulated by copper uptake, causing variable activity in various organs and tissue. This is particularly evident during blood production where copper is involved in haemoglobin synthesis (Avenant-Oldewage and Marx, 2000). For Zn, Shakweer and Abbas (1996) reported that the average concentrations of Zn were lower in the muscles of *Oreochromis niloticus* and *Sardinella aurita* than that in the livers, while Birungi *et al.* (2007) said that the relative accumulation of Zn in tissue of *Oreochromis niloticus* was of the order gills > liver > muscle. Working on *C. gariepinus*, Zn bioaccumulated in the different organs as: liver > skin > gills >

muscles (Gbem *et al.*, 2001); liver > gills > kidney > muscles (Abdel-Baky, 2001); liver > kidney > gills > skin > muscles (Rizkalla *et al.*, 2003) or gills > liver > kidney (Farombi *et al.*, 2007). Also, Rizkalla *et al.* (2003) indicated that the main sites of storing Zn are kidney and spleen for *Oreochromis* species and spleen for *Bagrus bayad* and the lowest Zn concentration is recorded in the muscles of all fish species. For Mn, Abdel-Baky (2001) said that the concentration of Mn in different organs of *C. gariepinus* followed a sequence of gills > liver > kidney > muscles. In general, Al-Nagaaway *et al.* (2009) mentioned that Fe, Zn and Cu concentrations in *Oreochromis niloticus* organs were in the following order: liver > gills > muscles.

CONCLUSION

From the findings of this study it is concluded that the essential heavy metals of interest found in measurable quantities are still within safe limits for consumption. The metal concentrations in fish are the result of complex processes associated with uptake, excretion rates and homeostasis in fish. Essential heavy metals cannot easily be defined due to a number of factors that can influence and modify the toxicity of these substances. Some of these factors include: the metal species in the water; the presence of other metals; abiotic factors (i.e. temperature, pH, dissolved oxygen, hardness, salinity, etc.); biotic factors (i.e. age, size and length of the fish, sex, stage in life history); feeding habits and behavioral responses. Through routine monitoring of the water at the sampling locations, the abiotic factors should be maintained at constant and acceptable levels and if this is not achieved, an increase in metal accumulation and toxicity would result which, ultimately, could be detrimental to the health of the fish. So, efforts should however be concentrated on ensuring that these concentrations are not exceeded. Safe disposal of domestic sewage and industrial effluents should be practiced and where possible recycled to avoid these metals and other contaminants from going into the environment. Laws enacted to protect our environment should be enforced.

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ARABIC SUMMARY

تباين قيم المعادن الثقيلة في أسماك القراميط المجمعة من شمال وجنوب منطقة القاهرة

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تم فى هذا البحث عمل مسح لمياه النيل خلال الفصول الأربعة (يناير - أبريل - يوليو - أكتوبر) لدراسة تجمع الحديد والنحاس والزنك و المنجنيز فى كل من الكبد والكلى والخياشيم والجلد والعضلات لسمكة قرموط النيل من منطقتين من النهر جنوب (العياط) وشمال (القناطر الخيرية) مدينة القاهرة. تم تحليل تركيزات العناصر بالأنسجة ثم إخضاع النتائج لمقارنة التركيزات فى منطقتى الدراسة وخلال المواسم الأربعة وأيضا بالنسبة لجنسى السمكة. لم يتم أستبيان أى أختلافات معنوية فى تركيزات العناصر بالمياة أثناء الفصول الأربعة وكانت أعلى القيم التى سجلت للحديد والنحاس أما أقلها فكانت للمنجنيز. وقد أوضحت الدراسة أن النحاس هو أكثر العناصر تائراً بالموقع وان تركيزة كان عالياً فى العياط عنه فى القناطر. ولم يلاحظ أى تأثير خطير للعناصر المدروسة على النظام البيئى. وبالنسبة لتركيزات العناصر فقد لوحظ أنها كانت أعلى بأنسجة سمكة القرموط عنها فى المياة التى تعيش فيها. وكانت تركيزات كل العناصر فى كل الأعضاء ذات قيم مسجلة ولكن فى الحدود الأمنة المسموحة للأستهلاك الأدمى. أوضحت تركيزات العناصر المدروسة لعدد كبير من القيم المعنوية وعلاقتها بالأختلافات بين موقع الدراسة وجنس السمكة والموسم. وتم التركيز فى كتابة مناقشة البحث على هذه الأختلافات المعنوية.